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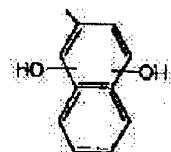
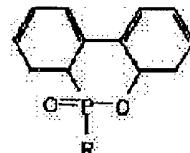
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(54) EPOXY RESIN COMPOSITION, ITS PRODUCTION, AND METALLIC FOIL WITH RESIN, AND MULTILAYER PRINTED WIRING BOARD USING THE METALLIC FOIL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition being a flame-retardant composition producing no harmful matter when burned, and capable of providing multilayer printed wiring boards excellent in heat resistance, etc., by including a specific compound, a specific epoxy resin and a specific crosslinked rubber.

SOLUTION: This composition is obtained by including (A) a phosphorus-containing compound of formula I (R is an organic group having 2 or more phenolic hydroxyl groups), (B) an epoxy resin having in the molecule ≤ 1.8 epoxy groups on average, pref. 1.8-2.5 epoxy groups (e.g. bisphenol A type epoxy resin), (C) a crosslinked rubber with a particle diameter of $\leq 1.0 \mu\text{m}$ pref. 0.5-0.02 μm (e.g. butadiene-acrylonitrile copolymer rubber). The group of formula II or formula III is desirable as the R of the compound of formula I. The amount of the component C to be added is desirable to be 0.2-15 phr, or more desirable to be 3-10 phr on a resin solid basis.



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TITLE: Epoxy resin composition which does not produce harmful material on burning, used for multilayered printed circuit board contains phosphorus-containing compound and crosslinked rubber particles

PATENT-ASSIGNEE: MATSUSHITA ELECTRIC WORKS LTD [MATW]

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ABSTRACTED-PUB-NO: JP2000256537A

BASIC-ABSTRACT:

NOVELTY - An epoxy resin composition contains:

- (A) phosphorus-containing compound,
- (B) epoxy resin having at least 1.8 epoxy groups and
- (C) crosslinked rubber having particle diameter of 1.0 micron or less.

DETAILED DESCRIPTION - An epoxy resin composition contains:

- (A) phosphorus-containing compound of formula (I),
- (B) epoxy resin having at least 1.8 epoxy groups in average and
- (C) crosslinked rubber having particle diameter of 1.0 micron or less.

R = organic group having at least 2 phenolic OH groups, preferably group of formula (II) or (III).

INDEPENDENT CLAIMS are also included for:

- (1) the preparation of the epoxy resin composition by reacting whole or a part

of epoxy resin with phosphorus-containing compound and then adding the other components to the reaction products; and

(2) a resin-attached metallic foil, which is prepared by applying the epoxy resin composition on a metallic foil and drying and finally, semi-curing the composition.

USE - The resin composition is useful for producing a multilayered printed circuit board.

ADVANTAGE - The resin composition does not produce harmful substance on burning.

CHOSEN-DRAWING: Dwg. 0/1

TITLE-TERMS: EPOXY RESIN COMPOSITION PRODUCE HARM MATERIAL BURN MULTILAYER PRINT CIRCUIT BOARD CONTAIN PHOSPHORUS CONTAIN COMPOUND CROSSLINK RUBBER PARTICLE

DERWENT-CLASS: A12 A21 A85 E11 L03 P73 V04 X12

CPI-CODES: A05-A01E2; A08-F; A08-R08B; A12-E07A; E05-G01; L03-H04E1;

EPI-CODES: V04-R07A; V04-R07L; X12-E02B;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

Fragmentation Code

B615 B701 B711 B720 B742 B815 B831 B840 D011 D016
D220 G015 G100 H4 H402 H442 H8 M280 M320 M411
M511 M520 M531 M540 M781 M904 M905 Q130 Q454 Q621
R038

Ring Index

40822

Specific Compounds

A2K46K A2K46U

Chemical Indexing M3 *02*

Fragmentation Code

B615 B701 B711 B720 B742 B815 B831 B840 D011 D016
D220 G001 G002 G014 G015 G016 G023 G040 G100 G221
H4 H402 H442 H8 M280 M320 M411 M511 M520 M531
M540 M781 M904 M905 Q130 Q454 Q621 R038

Ring Index

40822

Markush Compounds

200029-40801-K 200029-40801-U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P0464*R D01 D22 D42 F47 ; L9999 L2391 ; L9999 L2073 ; M9999
M2073

Polymer Index [1.2]

018 ; P1898*R P0464 D01 D10 D11 D18 D19 D22 D42 D76 F34 F47 ; L9999
L2391 ; L9999 L2073 ; M9999 M2073

Polymer Index [1.3]

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Polymer Index [1.4]

018 ; R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D83 F12

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the epoxy resin used for manufacture of a multilayer printed wiring board and a multilayer printed wiring board, its manufacture approach, and a metallic foil with resin using it further.

[0002]

[Description of the Prior Art] a current fire retardancy epoxy resin -- the autolysis nature -- good -- it has mechanical and electrical characteristics and is used for various electrical insulation materials. In order that the fire-resistant epoxy resin of these former may give fire retardancy to resin, a shaping constituent has autolysis nature by containing the halogen system compound which is mainly concerned with a bromine, and containing these, but when these constituents burn with a fire etc., under unfavorable conditions, the compound which has a bad influence on the bodies, such as dibenzo dioxin by which Pori bromination was carried out, and a furan, is formed. Furthermore, when the shaping constituent is heated, it is easy to disassemble a bromine, and a bromine content compound has bad thermal resistance over a long period of time. Therefore, there was a demand to the epoxy resin constituent which can attain the fire retardancy demanded without adding the halogen system compound which is mainly concerned with a bromine.

[0003] The method of applying and carrying out desiccation semi-hardening of the resin for an insulation, such as an epoxy resin constituent, to the metallic foil for electric conduction as the manufacture approach of a multilayer printed wiring board, carrying out laminate molding of the metallic foil with resin which forms an insulating layer and changes to the substrate for inner layers with which the circuit pattern was formed on the other hand, and manufacturing a multilayer printed wiring board is learned. However, this resin layer for an insulation that carried out semi-hardening had the case where the powder with which the resin layer broke when it was generally weak and the big force joined the resin layer in handling etc., and that resin layer broke separated from a metallic foil. And the resin layer broke, the multilayer printed wiring board manufactured using the metallic foil with resin which separated broke, or the cavity was generated in the insulating section of a part which separated, and there was a case where the insulation between a inner layer

circuit and an outer layer circuit fell. Moreover, when the metallic foil with resin in which the resin layer separated was used, there was a case where the powder with which the resin layer was fractured floated at the time of a laminating, adhered to the field of the side which does not form the resin layer for an insulation of a metallic foil, and a detailed resin hardened material was formed on the metallic foil for electric conduction of the laminate obtained. and the metallic foil for electric conduction of the outer layer on the front face of a laminate in which this resin hardened material was formed in order to manufacture a multilayer printed wiring board -- etching -- a conductor -- the ** into which the part in which the resin hardened material was formed is not etched when a circuit is formed -- remaining -- a conductor -- short [poor] may occur and the problem that the yield of a multilayer printed wiring board was low was also between circuits.

[0004] Therefore, by carrying out suitable amount combination into a resin constituent by using phenoxy resin and rubber non-constructing a bridge as a plasticity grant component, a resin constituent is made into flexible structure and making it hard for the resin layer for an insulation to break or to separate is examined. However, in the metallic foil with resin which blended such a plasticity grant component with the resin constituent for an insulation, there was a problem that the glass transition temperature of the resin hardened material obtained was low, and the thermal resistance of the multilayer printed wiring board which carried out laminate molding of them and manufactured them was low.

[0005] Therefore, the metallic foil with resin from which the multilayer printed wiring board in which the resin layer for an insulation breaks, could not separate easily, and thermal resistance was excellent is obtained is called for.

[0006]

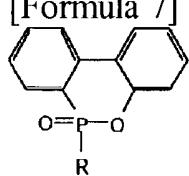
[Problem(s) to be Solved by the Invention] It is in offering the resin with which the multilayer printed wiring board in which this invention was made in view of the above problems, the place made into the purpose was a fire-resistant constituent which does not generate the matter harmful at the time of combustion, and the resin layer for an insulation breaks or could not separate easily when it was used for a metallic foil with resin and manufactured, and thermal resistance was excellent is obtained.

[0007]

[Means for Solving the Problem] That is, the epoxy resin constituent of this invention is the Lynn content compound (A) shown with the A following chemical formula A, and

[0008].

[Formula 7]



··· 化学式 A

[0009] (However, R is an organic radical which has two or more phenolic hydroxyl groups.)

B) The epoxy resin which has an average of 1.8 or more epoxy groups in intramolecular, and C particle diameter are 1.0. The bridge formation rubber below mum is contained as

an indispensable component.

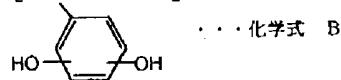
[0010]

[Embodiment of the Invention] For the epoxy resin constituent of this invention, particle diameter is [the specific Lynn content compound (A) which has a phenolic hydroxyl group, an epoxy resin, and] 1.0. Since the bridge formation rubber below mum is contained as an indispensable component The mold goods obtained from now on have fire retardancy, and have good flexibility in semi-hardening (B stage) resin and a hardened material with plasticity with this Lynn content compound, and the plasticity by bridge formation rubber, and its properties, such as thermal resistance, an electrical property, and a water resisting property, are also very better still.

[0011] When showing the Lynn content compound (A) of a chemical formula A is the radical expressed with chemical formulas B and C, especially in a hardened material, properties, such as thermal resistance, an electrical property, and a water resisting property, are still better with fire retardancy.

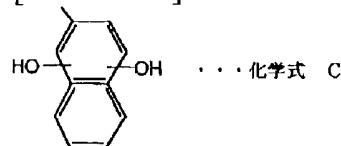
[0012]

[Formula 8]



[0013]

[Formula 9]



[0014] With bridge formation rubber, the secondary thing in the condition that functional groups, such as a carboxyl group and a glycidyl group, were distributed over front faces, such as conventional butadiene-acrylonitrile copolymerization rubber, is made to construct a bridge, and it grinds after that if needed. Although it does not limit especially as bridge formation rubber in this invention, what has the chemical presentation of SBR, BR, isobutylene isoprene rubber, etc. is used. When butadiene-acrylonitrile copolymerization rubber is used especially, while proper plasticity is acquired in B-stage resin and a hardened material, there is no fall of the glass transition point temperature after shaping (T_g), and the dispersibility to resin etc. is good.

[0015] Particle diameter is 1.0 as a rubber component. When larger bridge formation rubber than mum is used, dispersibility is bad and uniform plasticity is not acquired. Therefore, the more detailed one is desirable and particle diameter is 0.5. It is still more desirable if it is below mum. However, it is more desirable to be 0.02 micrometers or more, in order to obtain plasticity grant effectively. Moreover, when rubber non-constructing a bridge is used as a rubber component, the fall of the glass transition temperature after shaping (T_g) is intense, and the fall on the strength at the time of heating also has it. [intense]

[0016] Particle diameter is 1.0. The addition weight of the bridge formation rubber below

mum is 0.2 or more phrs and 15phr to resin solid content. When it is the following, while proper plasticity is acquired, there are few falls of the glass transition point temperature after shaping (Tg). 15phrs When many, the reinforcement of a resin hardened material falls, and the plasticization effectiveness is small when it is less than 0.2 phrs. They are 3phrs more preferably. It is 10phr above. It is the following.

[0017] Although the epoxy resin which has an average of 1.8 or more epoxy groups is used for intramolecular as an epoxy resin, when the epoxy resin (epoxy resin of two organic functions) which averages to intramolecular and has 1.8-2.5 epoxy groups (about two pieces) especially is used, the plasticization effectiveness of resin is also large. As an epoxy resin which averages to this intramolecular and has 1.8-2.5 epoxy groups (about two pieces), when the bisphenol A mold epoxy resin is used, it becomes good hardened materials, such as adhesive strength, fire retardancy becomes is easy to be acquired when a bisphenol female mold epoxy resin is used, and when the biphenyl mold epoxy resin expressed with a chemical formula D is used, water absorption is low and serves as a hardened material of high Tg. Moreover, a hardened material with high Tg is obtained by using the naphthalene mold epoxy resin expressed with a chemical formula E.

[0018] When the epoxy resin (epoxy resin of three organic functions) which averages to intramolecular as an epoxy resin and has 2.5-3.9 epoxy groups (about three pieces) is used, a hardened material with still higher Tg is obtained. If the epoxy resin which has the structure represented with a chemical formula F as an epoxy resin is used, low water absorption and a hardened material with the description of high Tg will be obtained.

[0019] Moreover, when a phenol novolak mold epoxy resin is used as an epoxy resin, it is high Tg and becomes the hardened material with which fire retardancy is easy to be acquired. An adhesive property, thermal resistance, electric insulation, Tg, etc. serve as a good hardened material of engine-performance balance by using a dicyandiamide as a curing agent of these epoxy resins. If polyvinyl-acetal resin is added and used for the epoxy resin constituent of this invention, plasticity can be further given to B-stage resin and a hardened material, even when it is used for a metallic foil with resin, a resin layer will break, or the powder of resin will stop being able to fall easily.

[0020] The Lynn quantitative formula of these epoxy resin constituents is 0.8-5.0 of the whole resin solid content. When it is weight %, good fire retardancy is acquired. For the optimal Lynn quantitative formula, although it changes with epoxy resins to be used, the Lynn quantitative formula is 0.8 of the whole resin solid content. The case of under weight %, the stable fire retardancy is hard to be acquired and it is 5.0. When exceeding weight %, the property of a hardened material gets worse or the dispersibility of a bridge formation rubber component gets worse. It is 1.2 - 2.5 % of the weight more preferably. the value converted into the content of the Lynn atom with the Lynn quantitative formula here -- it is -- for example, the matter of molecular weight 324 -- the Lynn atom -- those with one piece, and this matter -- 50wt(s)% -- if it is the combination to include, it will become the 4.78wt% Lynn quantitative formula (since the atomic weight of the Lynn atom is about 31, it is $31/324 \times 0.5 = 0.0478$).

[0021] Into the epoxy resin constituent of this invention, a copper foil pattern is floated up in the shape of a silhouette in the case of inspection after circuit formation of the multilayer

printed wiring board manufactured by containing the chemical which emits fluorescence by ultraviolet rays etc., or resin using the resin constituent, this recognizes a pattern configuration, and it becomes easy to conduct visual inspection. In case the resin constituent of this invention is manufactured, when the heatproof of a hardened material and a waterproof property improve sharply by using accelerators, such as tertiary amine or triphenyl phosphine, heating the Lynn content compound (A) which has all, or some epoxy resins and phenolic hydroxyl groups, making it react beforehand (preliminary reaction), and blending other components, i.e., bridge formation rubber, the remaining epoxy resins, etc., after that, the preservation stability of B stage-sized resin becomes good. That is, since a viscosity rise of the resin at the time of a mothball is suppressed, even if it carries out a long term storage in the condition, such as a metallic foil with resin, there is no aggravation of a moldability etc.

[0022] this preliminary reaction -- epoxy group 1.0 of an epoxy resin receiving -- the phenolic hydroxyl group 0.3-1.0 of the Lynn content compound (A) -- more -- desirable -- 0.4-0.8 It is not this limitation, although it is desirable to carry out by the mole fraction in order to obtain preservation stability and a good hardened material. Moreover, the epoxy resin used for this preliminary reaction has the desirable epoxy resin of two organic functions or three organic functions, and when an epoxy resin with few these functional groups is used for a preliminary reaction, the product stabilized especially is obtained.

[0023] In case these epoxy resin constituents are obtained, a solvent may be used and a non-solvent may perform. In case these epoxy resin constituents are obtained, a hardening accelerator and other property grant agents may be added if needed. Thus, using comma coater, an imprint coating machine, curtain coater, die coater, etc., the obtained epoxy resin constituent is applied to metallic foils, such as copper foil and aluminum foil, carries out continuation or non-per-continuum stoving, and is formed into B stage, an insulating layer is formed, and a metallic foil with resin is obtained.

[0024] The metallic foil thickness in this case and insulating-layer resin thickness are 8 as a metallic foil, although it is arbitrary. As mum-80micrometer and insulating-layer resin thickness, it is 20micrometer-200. mum is common. A resin side is made to counter both sides or one side of the substrate for inner layers, a laminating is carried out to it, hot forming is carried out to it, circuit formation of an outer layer is performed further, and a multilayer printed wiring board is obtained. [finishing / circuit pattern formation / metallic foil / above-mentioned / with resin]

[0025]

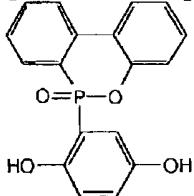
[Example] The raw material shown below was used in the following examples and examples of a comparison.

- epoxy resin 1: -- bisphenol A mold 2 organic-functions epoxy resin [of weight per epoxy equivalent 190]; -- product made from oil-ized Shell Epoxy trade name Epicoat 828 and epoxy resin 2: -- bisphenol female mold 2 organic-functions epoxy resin [of weight per epoxy equivalent 172]; -- product made from Dainippon Ink Industry trade name EPICLON-830 and epoxy resin 3: -- biphenyl mold 2 organic-functions epoxy resin [of weight per epoxy equivalent 195]; -- product made from oil-ized Shell Epoxy trade name YX4000H and epoxy resin 4: -- naphthalene mold 2 organic-functions epoxy resin [of

weight per epoxy equivalent 150]; -- the Dainippon Ink industry Make trade name EPICLON-HP4032 and epoxy resin 5: -- 3 organic-functions mold epoxy resin [of weight per epoxy equivalent 210]; -- Mitsui Chemicals, Inc. make Trade name VG 3101 (compound which has the structure of a chemical formula F)

- epoxy resin 6: -- phenol novolak mold epoxy resin [of weight per epoxy equivalent 190]; -- product made from Dainippon Ink Industry trade name EPICLON-770 and epoxy resin 7: -- 4 organic-functions epoxy resin; which emits the fluorescence of weight per epoxy equivalent 220 -- product made from U.S. Shell Trade name Epon1031 and epoxy resin 8: bromination bisphenol A mold epoxy resin [of weight per epoxy equivalent 400] (rate of bromination = about 48 wt(s)%); -- Tohto Kasei Co., Ltd. make trade name YDB400 and epoxy resin 9: -- cresol novolak mold epoxy resin [of weight per epoxy equivalent 220]; -- Tohto Kasei Co., Ltd. make Trade name YDCN704 and curing agent 1: The reagent dicyandiamide molecular weight 84, theoretical active hydrogen equivalent =21 g/eq and curing agent 2:hydroxyl equivalent 105 g/eq, phenol novolak resin with a melting point of about 80 degrees C; Gunei Chemical Industry Co., Ltd. make Trade name PSM6200 and the Lynn content compound 1 : In a chemical formula A The following compound whose R is a chemical formula B [0026]

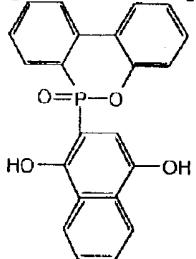
[Formula 10]



[0027] Lynn content = -- about 9.6 wt(s)% -- made in Sanko Trade name HCA-HQ (hydroxyl equivalent about 162 g/eq)

- Lynn content compound 2 : the following compound Lynn content =about 8.2 wt(s)% whose R is a chemical formula C in a chemical formula A [0028]

[Formula 11]



[0029] Made in Sanko Trade name HCA-NQ (hydroxyl equivalent about 188 g/eq) Lynn content compound 3 : - A phenolic hydroxyl group The Lynn content compound which have and is not; Asahi Denka Kogyo K.K. make The trade name ADEKA stub PFR, Lynn content = abbreviation 9.8wt% and particle bridge formation rubber : It is bridge formation rubber of butadiene-acrylonitrile copolymerization rubber (thing over which the secondary carboxyl group distributed over a front face was made to construct a bridge). Rubber with a particle diameter of 0.5 micrometers or less; Japan Synthetic Rubber Co.,

Ltd. make Trade-name XER-91 and rubber non-conducting a bridge: Japan Synthetic Rubber Co., Ltd. make Trade name N220SH (it is equivalent to the non-conducting bridge rubber article of the above-mentioned particle bridge formation rubber)

- Polyvinyl-acetal resin : DENKI KAGAKU KOGYO K.K. make Trade-name 6000AS and a solvent 1: Reagent Methyl ethyl ketone (MEK)
- Solvent 2 : reagent Methoxy propanol (MP)
- Solvent 3 : reagent Dimethylformamide (DMF)
- Preliminary reaction epoxy resin 1 : they are weight-per-epoxy-equivalent about 540 g/eq, and about 40 150-degree-C melt viscosity poise(s) by carrying out heating stirring of an epoxy resin 1 (70 weight sections) and the Lynn content compound 1 (30 weight sections) within a flask at 130 degrees C with a non-solvent, and continuing [the triphenylphosphine of the reagent as an accelerator] addition and about 3-hour heating stirring for the 0.2 weight section after that. The Lynn content about 2.9 wt(s)% epoxy resin was obtained.

[0030] - Preliminary reaction epoxy resin 2 : they are weight-per-epoxy-equivalent about 580 g/eq, and about 100 150-degree-C melt viscosity poise(s) by carrying out heating stirring of an epoxy resin 2 (70 weight sections) and the Lynn content compound 1 (30 weight sections) within a flask at 130 degrees C with a non-solvent, and continuing [the triphenylphosphine of the reagent as an accelerator] addition and about 4-hour heating stirring for the 0.2 weight section after that. The Lynn content about 2.5 wt(s)% epoxy resin was obtained.

[0031] The following examples and examples of a comparison are the approaches shown below, and performed shaping, evaluation, etc.

<Manufacture of an epoxy-resin constituent> A law: The particle bridge formation rubber distributed to homogeneity at about 20 wt(s)% at the methyl-ethyl-ketone solution, the Lynn content compound and an epoxy resin, and other additives were beforehand fed into the predetermined solvent, and it mixed by about 1000 rpm by the "homomixer" by the special machine processing industrial company for about 90 minutes. Then, a hardening accelerator (reagent 2-ethyl-4- methyl imidazole) is blended, and it stirs again for about 15 minutes, it deaerates after that, and is about 500 to 1000 poise at 25 degrees C. The resin varnish was obtained.

B law: The preliminary reaction epoxy resin of point ** was manufactured, and beforehand, other epoxy resins and other additives were fed into the predetermined solvent its after that and preliminary reaction epoxy resin, the particle bridge formation rubber distributed to homogeneity at about 20 wt(s)% at the methyl-ethyl-ketone solution, and if needed [the Lynn content compound and if needed], and it mixed by about 1000 rpm by the "homomixer" by the special machine processing industrial company for about 90 minutes. Then, a hardening accelerator (reagent 2-ethyl-4- methyl imidazole) is blended, and it stirs again for about 15 minutes, it deaerates after that, and is about 500 to 1000 poise at 25 degrees C. The resin varnish was obtained.

As <manufacture of copper foil with resin> copper foil, the copper foil (the trade name GT made from Koga Circuit Foil) of thickness 0.018 mm was used.

[0032] Moreover, the coating of resin and the osmosis approach were performed by the

following methods of construction. By carrying out coating of various kinds of epoxy resin constituents by the comma coating machine at a room temperature to the roughening side of copper foil, and heating them at about 130-170 degrees C by the non-contact type heating unit after that to it, dried the solvent, resin was made to form into B stage to the level suitable for shaping, and copper foil with resin of 75-85 micrometers of resin thickness was obtained.

< evaluation-criteria > 1. -- -proof -- melanism -- processing adhesive strength -- the copper foil with resin manufactured as mentioned above by 0.2mm in thickness The inner layer core double-sided plate (Matsushita Electric Works CR1766, 35 micrometers of copper foil thickness) which performed inner layer processing (melanism processing) which mentions surface copper foil later is used as an inner strake. They are about 30 kgf/cm², heating the 170 degrees C of the one above-mentioned copper foil with resin of this inner strake up and down at a time in piles for 90 minutes. It pressurized and fabricated.

[0033] the melanism of a inner layer of the above-mentioned shaping plate -- adhesive strength with a processing plate was evaluated by 25 degrees C with the Peel test method 90 degrees. (JIS C6481)

[Copper foil processing of a inner layer core double-sided plate (melanism processing)] processing liquid: -- what oxidized 95 degrees C of double-sided copper foil for 60 seconds in the water solution of the water-solution above of sodium chlorite 50 g/L, sodium-hydroxide 10 g/L, and phosphoric-acid 3 sodium 10 g/L -- melanism -- it considered as the processing plate and used for the inner strake.

2. They are about 30 kgf/cm², heating the 170 degrees C of the one above-mentioned copper foil with resin of this inner strake up and down at a time in piles for 90 minutes by using as an inner strake the fire-resistant inner layer core double-sided plate (Matsushita Electric Works CR1766) from which surface copper foil was completely removed for the copper foil with resin which is the fire-resistant evaluation above, and was made and manufactured by 0.2mm in thickness. It pressurized and fabricated. The copper foil of the front face of this shaping plate was removed, it cut in die length of 125mm, and width of face of 13mm, and combustion behavior was tested according to "Test for Flammability of Plastic Materials-UL94" of Under WritersLaboraoriess. Moreover, in order to grasp an antiphlogistic difference, the mean time to resolution has been grasped.

3. The resin side side was fabricated for the copper foil with resin which is the evaluation above of water absorption, and was made and manufactured like lamination and the above, copper foil was removed after that, and the hardened material with a resin thickness of about 160 micrometers was obtained. This hardened material was cut in die length of 500mm, and width of face of 400mm, it boiled at 100 degrees C for 2 hours, and the coefficient of water absorption was measured.

[0034] Water absorption = (weight before the weight-water absorption after water absorption) weight x1004. glass transition temperature before /water absorption (Tg) The above-mentioned sample for water absorption evaluation was cut in die length of 30mm, and width of face of 5mm, tan delta was measured with viscoelasticity spectrometer equipment, and the peak temperature was set to Tg.

Copper Foil with Resin Which is Heat-resistant above, and was Made and Manufactured

5. By 0.2Mm in Thickness The inner layer core double-sided plate (Matsushita Electric Works CR1766, 35 micrometers of copper foil thickness) which performed above-mentioned inner layer processing (melanism processing) for surface copper foil is used as an inner strake. They are about 30 kgf/cm², heating the 170 degrees C of the one above-mentioned copper foil with resin of this inner strake up and down at a time in piles for 90 minutes. It pressurized and fabricated.

[0035] This sample was cut to 50mmx50mm, the sample of four sheets was prepared, it heated in oven for 60 minutes, abnormalities in an appearance, such as blistering of a multilayer board, were evaluated, and the temperature which became an excellent article four sheets has been grasped.

6. The copper foil with resin which is the resin preservation stability above of copper foil with resin, and was made and manufactured was left in the 40-degree C dryer, it was failed to shave only the resin, and 130-degree C melt viscosity evaluated the time amount which increases 50% to initial value.

7. The copper foil with resin which is the resin crack include-angle above of copper foil with resin, and was made and manufactured was cut in width of face of 100mm, and like drawing 1, bending and the minimum include angle from which the crack (crack) of resin arises were evaluated so that a trough chip box might come copper foil.

8. The resin side was made to counter on the substrate [finishing / circuit pattern formation / copper foil / which is the inspection ease above of a multilayer board detailed circuit, and was made and manufactured / with resin] for inner layers, the laminating was carried out, hot forming was carried out, circuit formation of the copper foil of an outer layer was performed further, and the multilayer printed wiring board was manufactured. Pattern configuration inspection of the circuit was carried out, the ease was compared, and O and x estimated.

9. The content of the main halogens, such as Cl and Br, was measured with halogen content X-ray fluorescence equipment.

The result evaluated by the approach of point ** is shown in Tables 1-3 about the copper foil with resin of the various resin manufactured by the manufacture approach of the copper foil with resin of examples 1-16, the example 1 of a comparison - 6 point **. the combination weight section of each component -- the inside of () -- weight per epoxy equivalent -- < -- the inside of > -- the phenol nature hydroxyl equivalent of the Lynn content compound -- < -- In >, it was shown, respectively.

[0036]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6
エボキシ樹脂	エボキシ樹脂1 (4.7) <0, 2.5>	エボキシ樹脂2 (4.7) <0, 2.7>	エボキシ樹脂3 (4.7) <0, 2.4>	エボキシ樹脂4 (4.7) <0, 3.1>	エボキシ樹脂5 (4.7) <0, 2.2>	エボキシ樹脂1 (4.7) <0, 2.5>
エボキシ樹脂6	エボキシ樹脂6 (5.3) <0, 2.8>	エボキシ樹脂7 (7) <0, 0.23>				
-	-	-	-	-	-	エボキシ樹脂6 (4.8) <0, 2.5>
- 合計「エボキシ当量」	0. -5.3	0. -5.5	0. -5.2	0. -5.9	0. -5.0	0. -5.2
リン含有化合物1	リン含有化合物1 (2.0) <0, 1.2>					
触媒擴張子ム	(7)	(7)	(7)	(7)	(7)	(7)
硬化剤	1 (4, 3)	1 (4, 5)	1 (4, 2)	1 (4, 9)	1 (4, 0)	1 (4, 2)
溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)
溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)
溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)
硬化促進剤	2-イソブ-4-チル ビニル-4-試験 (0, 1.0)					
その他添加剤	-	-	-	-	-	-
接着ワニス製造法	A法	A法	A法	A法	A法	A法
対固形分中リ含有量	1. 5wt%					
電極性	V-0	V-0	V-0	V-0	V-0	V-0
(平均消炎時間)	(2, 5秒)	(1, 5秒)	(2, 5秒)	(2, 5秒)	(3, 5秒)	(2, 5秒)
対黒化処理	1, 2	1, 0	1, 2	1, 0	1, 0	1, 2
接着力 (kgf/cm)	2. 5	2. 8	1. 7	1. 8	1. 8	2. 5
吸水力 (wt%)	160	150	170	180	190	165
Tg (°C)	240	240	240	240	240	240
耐熱性 (°C)	5日	6日	5日	4日	5日	5日
相溶性評定性	3.5	3.5	3.5	3.5	3.5	3.5
接着剤角度(度)	1wt%以下	1wt%以下	1wt%以下	1wt%以下	1wt%以下	1wt%以下
0.05%含有率(wt%)	X	X	X	X	X	O
回路ハーネス検査容易性						

[0037]
[Table 2]

	実施例7	実施例8	実施例9	実施例10	実施例11	実施例12
エボキシ樹脂	エボキシ樹脂1 (4.7)<0.25> エボキシ樹脂6 (5.3)<0.28>	エボキシ樹脂4 (4.7)<0.31> エボキシ樹脂6 (5.3)<0.28>	エボキシ樹脂1 (4.7)<0.25> エボキシ樹脂6 (5.3)<0.28>	エボキシ樹脂6 (5.3)<0.28> (予備反応物)	エボキシ樹脂6 (5.3)<0.28>	エボキシ樹脂6 (5.3)<0.28> (予備反応物)
リン含有化合物	リン含有化合物2 (2.4)<0.13>	リン含有化合物1 (2.1)<0.13>	リン含有化合物1 (6.0)<0.37>	リン含有化合物1 (6.7)	リン含有化合物1 (6.7)	リン含有化合物1 (6.7)
着色剤-ゴム	着色剤(7)	(7)	(7)	(7)	(7)	(7)
硬化剤	1(4.3)	1(4.2)	1(1.6)	1(4.2)	1(4.2)	1(4.2)
溶媒1(5.0)	溶媒1(5.0)	溶媒1(5.0)	溶媒1(5.0)	溶媒1(5.0)	溶媒1(5.0)	溶媒1(5.0)
溶媒2(5.0)	溶媒2(5.0)	溶媒2(5.0)	溶媒2(5.0)	溶媒2(5.0)	溶媒2(5.0)	溶媒2(5.0)
溶媒3(5.0)	溶媒3(5.0)	溶媒3(5.0)	溶媒3(5.0)	溶媒3(5.0)	溶媒3(5.0)	溶媒3(5.0)
硬化促進剤	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)	2-イソブチル-4-フェノール イミダゾール-4-試薬 (0.10)
その他添加剤	-	*リビドウ-474-4	-	-	-	-
樹脂ワニス製造法	A法	A法	B法	B法	B法	B法
対固形分中リビドウ量	1.5wt%	1.5wt%	3.5wt%	1.5wt%	1.5wt%	1.5wt%
(平均消炎時間)	V-0 (2.5秒)	V-0 (2.5秒)	V-0 (0.5秒)	V-0 (2.5秒)	V-0 (3.0秒)	V-0 (2.5秒)
抗黒化処理	1.0	1.0	0.9	1.3	1.5	1.3
接着力(kgf/cm)	2.0	3.0	4.0	1.9	1.5	1.9
吸水力(wt%)	1.65	1.60	1.10	1.60	1.80	1.60
Tg(°C)	240	240	240	245	245	245
耐熱性	樹脂保存安定性 5日	6日	6日	12日	14日	12日
樹脂割れ角度(度)	3.5	4.5	3.5	3.8	4.2	4.5
1wt%含有率(wt%)	1wt%以下	1wt%以下	1wt%以下	1wt%以下	1wt%以下	1wt%以下
回路バインディング容易性	x	x	x	x	x	x

[0038]
[Table 3]

実施例	実施例13		実施例14		実施例15		実施例16		実施例17		実施例18	
	エボキシ樹脂	(5.3) <0, 2.8>	エボキシ樹脂6 (3.5) <0, 1.8>	エボキシ樹脂6 (3.5) <0, 1.8>	エボキシ樹脂6 (3.5) <0, 2.8>	エボキシ樹脂6 (3.5) <0, 2.4>	エボキシ樹脂9 (3.5) <0, 1.8>	エボキシ樹脂9 (3.5) <0, 1.8>	エボキシ樹脂9 (3.5) <0, 1.2>	エボキシ樹脂9 (3.5) <0, 1.2>	エボキシ樹脂6 (3.5) <0, 1.6>	エボキシ樹脂6 (3.5) <0, 1.6>
(予備反応物)	<0, 1.6>	(予備反応物)	<0, 1.6>	(予備反応物)	<0, 1.6>	(予備反応物)	<0, 1.2>	(予備反応物)	<0, 1.2>	(予備反応物)	<0, 1.6>	(予備反応物)
-	-	-	-	(予備反応物)	-	-	-	-	-	-	-	-
- 合計エボキシ当量	0. 40	0. 34	0. 40	0. 49	0. 40	0. 49	0. 40	0. 40	0. 36	0. 36	0. 34	0. 34
リン含有化合物	予備反応性キシ1											
微細架橋ゴム	(2)	(2)	(8.5)	(4.0)	(6.7)	(7)	(7)	(7)	(7)	(7)	(7)	(7)
硬化剤	1 (4, 2)	1 (3, 6)	1 (5, 1)	1 (4, 2)	1 (3, 8)	1 (5, 1)	1 (4, 2)	1 (4, 2)	1 (3, 8)	1 (3, 8)	1 (3, 5)	1 (3, 5)
溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)	溶媒1 (5.0)
溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)	溶媒2 (5.0)
溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)	溶媒3 (5.0)
硬化促進剤	2-ブチ-4-チル ジアツ-4-試薬 (0, 10)											
その他添加剤	-	-	-	-	-	-	-	-	-	-	-	-
樹脂ワニス製造法	B法											
対固形分中合有量	1. 5wt%	1. 9wt%	0. 9wt%	1. 5wt%								
燃焼性 (平均燃焼時間)	V-0 (2, 5秒)	V-0 (0, 8秒)	V-0 (4, 5秒)	V-0 (2, 0秒)	V-0 (2, 0秒)	V-0 (2, 0秒)	V-0 (2, 0秒)	V-0 (4, 0秒)	V-0 (4, 0秒)	V-0 (4, 0秒)	V-0 (1, 5秒)	V-0 (1, 5秒)
対凍化處理 接着力 (kgf/cm)	1. 3	1. 2	1. 2	1. 2	1. 2	1. 2	1. 2	1. 3	1. 3	1. 3	0. 5	0. 5
吸水力 (wt%)	1. 6	2. 0	2. 0	2. 0	2. 0	2. 0	2. 0	2. 5	1. 9	1. 9	1. 60	1. 60
Tg (°C)	163	158	158	158	158	158	158	160	155	155	160	160
耐熱性 (℃)	245	245	245	245	245	245	245	245	245	245	245	245
油脂保存安定性 油脂離れ角度 (度)	13日	12日	12日	12日	7日	7日						
耐候性 (WT%)	3.0	4.0	3.5	3.5	3.5	3.5	3.5	5.0	4.0	4.0	3.8	3.8
回路パターン検査容易性	X	X	X	X	X	X	X	X	X	X	X	X

[0039]
[Table 4]

	比較例 1 エボキシ樹脂 (5.0) <0. 13>	比較例 2 エボキシ樹脂 8 (4.7) <0. 25>	比較例 3 エボキシ樹脂 1 (4.7) <0. 25>	比較例 4 エボキシ樹脂 1 (4.7) <0. 25>	比較例 5 エボキシ樹脂 1 (4.7) <0. 25>	比較例 6 エボキシ樹脂 1 (4.7) <0. 25>
エボキシ樹脂 エボキシ樹脂 6 (5.0) <0. 26>	エボキシ樹脂 6 (5.3) <0. 28>					
合計エボキシ当量	-	-	-	-	-	-
リン含有化合物	-	-	-	-	-	-
微細架橋ゴム	(7)	(7)	(0)	(7)	(0)	(7)
硬化剤	1 (4. 0) 溶媒1 (4.0) 溶媒2 (4.0) 溶媒3 (4.0)	1 (5. 5) 溶媒1 (4.0) 溶媒2 (4.0) 溶媒3 (4.0)	1 (5. 5) 溶媒1 (4.0) 溶媒2 (4.0) 溶媒3 (4.0)	1 (5. 5) 溶媒1 (5.0) 溶媒2 (5.0) 溶媒3 (5.0)	1 (4. 3) 溶媒1 (5.0) 溶媒2 (5.0) 溶媒3 (5.0)	1 (4. 3) 溶媒1 (5.0) 溶媒2 (5.0) 溶媒3 (5.0)
硬化促進剤	2-ブチ-4-フタ 4ヒドロ-4-試素 (0, 10)					
その他添加剤	-	-	-	-	-	-
樹脂ワニス製造法	-	-	-	A法	A法	A法
対固形分中リン含有量	0. 0wt%	0. 0wt%	0. 0wt%	2. 0wt%	1. 5wt%	1. 5wt%
燃焼性 (平均燃焼時間)	V-0 (3. 0秒)	H-B (燃焼)	H-B (燃焼)	V-1 (9. 0秒)	V-0 (2. 5秒)	V-0 (2. 5秒)
対黒化処理 接着力 (kgf/cm)	1. 2 (3. 0秒)	1. 0 (燃焼)	1. 0 (燃焼)	1. 2 (9. 0秒)	1. 2 (2. 5秒)	1. 2 (2. 5秒)
Tg (℃)	3. 0 140 225	3. 2 140 235	3. 0 140 235	5. 0 100 210	2. 5 160 240	3. 5 143 225
措施保存安定性 油脂離れ角度(度)	12日 15	12日 15	12日 15	8日 15	5日 15	5日 25
耐熱性 B-T=約230t% 回路ループ検査容易性	1wt%以下 X	1wt%以下 X	1wt%以下 X	1wt%以下 X	1wt%以下 X	1wt%以下 X

[0040] In addition, since rubber non-constructing a bridge was blended in the example 6 of a comparison, compared with the bridge formation rubber combination article (example 1), the degree of hardness at the time of heat (100 degrees C) was low 30%.

[0041]

[Effect of the Invention] Like this invention, by using an epoxy resin, and the special Lynn content compound (A) and detailed bridge formation rubber, it has fire retardancy, without having flexibility in B stage condition and a hardened material, and containing a halogenated compound, and the resin which was moreover excellent in thermal resistance or its metallic foil with resin, the laminate using this, and a multilayer board can be obtained.

[Translation done.]

* NOTICES *

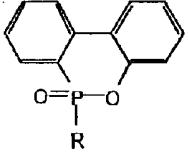
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A) The Lynn content compound (A) shown with the following chemical formula A, [Formula 1]

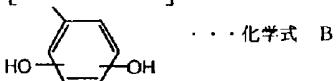


··· 化学式 A

(However, R is an organic radical which has two or more phenolic hydroxyl groups.)
B) The epoxy resin which has an average of 1.8 or more epoxy groups in intramolecular, and C particle diameter are 1.0. Epoxy resin constituent which contains the bridge formation rubber below mum as an indispensable component.

[Claim 2] The epoxy resin constituent according to claim 1 whose R of said chemical formula A is the radical expressed with the following chemical formula B.

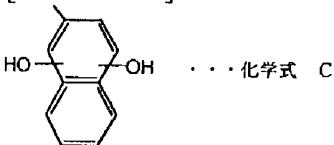
[Formula 2]



··· 化学式 B

[Claim 3] The epoxy resin constituent according to claim 1 whose R of said chemical formula A is the radical expressed with the following chemical formula C.

[Formula 3]



··· 化学式 C

[Claim 4] Said particle diameter is 1.0. Epoxy resin constituent according to claim 1 to 3 using butadiene-acrylonitrile copolymerization rubber as bridge formation rubber below mum.

[Claim 5] Said particle diameter is 1.0. The addition weight of the bridge formation rubber below mum is 0.2 or more phrs and 15phr to resin solid content. Epoxy resin constituent

according to claim 1 to 4 which is the following.

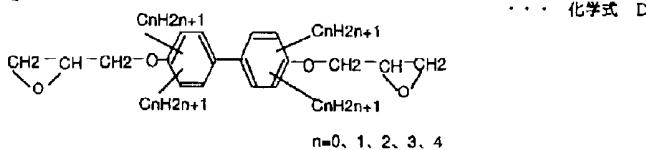
[Claim 6] The epoxy resin constituent according to claim 1 to 5 using the epoxy resin which averages to intramolecular and has 1.8-2.5 epoxy groups as said epoxy resin.

[Claim 7] The epoxy resin constituent according to claim 6 using the bisphenol A mold epoxy resin as an epoxy resin which averages to said intramolecular and has 1.8-2.5 epoxy groups.

[Claim 8] The epoxy resin constituent according to claim 6 using a bisphenol female mold epoxy resin as an epoxy resin which averages to said intramolecular and has 1.8-2.5 epoxy groups.

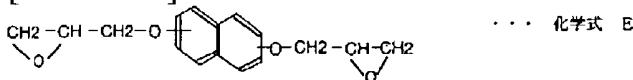
[Claim 9] The epoxy resin constituent according to claim 6 using the biphenyl mold epoxy resin expressed with the following chemical formula D as an epoxy resin which averages to said intramolecular and has 1.8-2.5 epoxy groups.

[Formula 4]



[Claim 10] The epoxy resin constituent according to claim 6 using the naphthalene mold epoxy resin expressed with the following chemical formula E as an epoxy resin which averages to said intramolecular and has 1.8-2.5 epoxy groups.

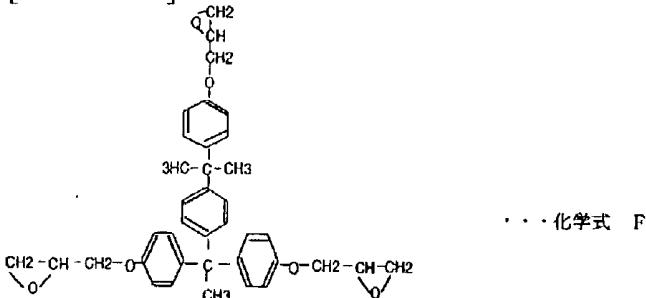
[Formula 5]



[Claim 11] The epoxy resin constituent according to claim 1 to 5 using the epoxy resin which averages to intramolecular and has 2.5-3.9 epoxy groups as said epoxy resin.

[Claim 12] The epoxy resin constituent according to claim 1 to 5 using the epoxy resin which has the structure represented with the following chemical formula F as said epoxy resin.

[Formula 6]



[Claim 13] The epoxy resin constituent according to claim 1 to 5 using a phenol novolak mold epoxy resin as said epoxy resin.

[Claim 14] The epoxy resin constituent according to claim 1 to 13 using a dicyandiamide as a curing agent of an epoxy resin.

[Claim 15] The epoxy resin constituent according to claim 1 to 14 which contains

polyvinyl-acetal resin as an indispensable component.

[Claim 16] The Lynn quantitative formula is 0.8-5.0 of the whole resin solid content.

Epoxy resin constituent according to claim 1 to 15 which is weight %.

[Claim 17] The epoxy resin constituent containing the constituent or resin which emits fluorescence in an epoxy resin constituent according to claim 1 to 16.

[Claim 18] The manufacture approach of the epoxy resin constituent according to claim 1 to 17 which is the manufacture approach of an epoxy resin constituent according to claim 1 to 17, and blends other components after making all, or some epoxy resins and the Lynn content compounds (A) react beforehand.

[Claim 19] The metallic foil with resin which applies the epoxy resin constituent of a publication, or the epoxy resin constituent manufactured by the manufacture approach of claim 18 on a metallic foil, and is obtained by carrying out desiccation semi-hardening by either of claims 1-17.

[Claim 20] The metallic foil with resin according to claim 19 using copper foil as said metallic foil.

[Claim 21] The multilayer printed wiring board which comes to carry out laminate molding of the metallic foil with resin according to claim 19 or 20 to the substrate [finishing / circuit pattern formation] for inner layers.

[Translation done.]